Photoinduced Molecular Transformations. Part 144.[1] One-carbon Intercalation of γ- and δ-Lactones involving the β-Scission of Alkoxyl Radicals as the Key Step: Synthesis of δ- and ε-Lactones with α-Substituents

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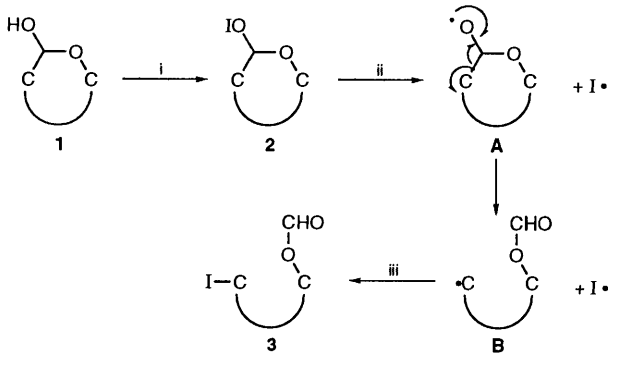
A new general method for a one-carbon intercalation of γ-lactones to δ-lactones and δ-lactones to ε-lactones in three steps involving a selective β-scission of the alkoxyl radicals as the key step is described. The reactions of γ- and δ-lactones with lithioalkyl acetate gave an equilibrated mixture of alkyl (2-hydroxytetrahydrofuran-2-yl)acetates and alkyl (2-hydroxytetrahydropyran-2-yl)acetates, as well as their ring-opened isomers in 62–95% yields, respectively. The photolysis of the hypoiodites of these lactols in benzene containing mercury(II) oxide and iodine with Pyrex-filtered light resulted in a selective endocyclic β-scission of the corresponding alkoxyl radicals to give alkyl iodoalkyl propanedioates in 33–70% yields. Treatment of the iodoalkyl propanedioates with tetraethylammonium bromide and sodium hydride gave alkyl 3,4,5,6-tetrahydro-2-oxo-2*H*-pyran-3-carboxylates or alkyl 2,3,4,5,5a,6,7,8,9,9a-decahydro-2-oxobenz[1]oxepine-3-carboxylate in 61–81% yields. On the other hand, successive treatment of ω-iodoalkyl propanedioates with tetraethylammonium bromide–sodium hydride and then benzyl bromide gave a α-disubstituted δ-lactone, which gave a α-monosubstituted δ-lactone upon heating in trifluoroacetic acid under reflux. Cyclopentanone can similarly be transformed into 2-substituted cyclohexanone *via* a three-step procedure.

We reported in earlier papers of this series that the irradiation of the hypoiodites **2** generated *in situ* from lactols **1** with an excess of mercury(II) oxide and iodine with Pyrex-filtered light resulted in a selective β-scission of the C–C bond of the corresponding alkoxyl radicals **A** to give iodo formates **3** *via* the carbon-centred radical **B**, as outlined in Scheme 1.[2] We have



Scheme 1 *Reagents and conditions:* i, $HgO + I_2 \rightarrow I_2O$; ii, *hν*; iii, **2** or I_2

also demonstrated in this and subsequent papers that a variety of saturated heterocycles such as cyclic ethers, cyclic sulfides, cyclic amines, cyclic tellurides and cyclic selenides can be prepared from the iodo formates derived by the β-scission of the alkoxyl radicals.[3]

In this paper we report on a further application of this selective β-scission of the C–C bond of the alkoxyl radicals generated from the substituted five- and six-membered lactol hypoiodites to a one-carbon intercalation of the γ- and δ-lactones *via* three-steps (Scheme 2).

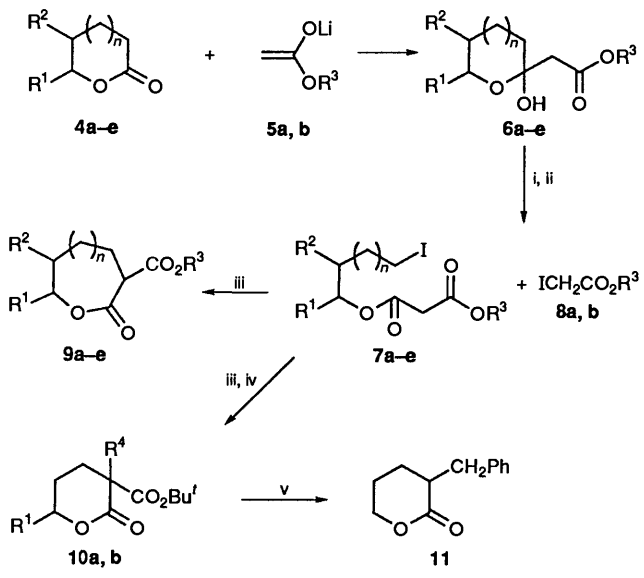
Ring-expansion reactions are among the most useful methodologies for the preparation of medium- to large-membered rings in organic synthesis.[4] Thus, a variety of methods for the ring expansion of cyclic ketones, such as the Tiffeneau–Demjanow ring expansion,[5] diazomethane homologation[6] and others,[7] have been available. Methods, for the ring expansion of lactones, however, have been little reported.[8]

Preparation of Substrates for Intercalation.—*tert*-Butyl (2-hydroxytetrahydrofuran-2-yl)acetate **6a**[9] and *tert*-butyl (2-hydroxy-3,4,5,6-tetrahydropyran-2-yl)acetate **6d**,[9] reported by Dugan *et al.* from the reaction of γ-butyrolactone and δ-valerolactone with *tert*-butyl acetate lithium enolate, were chosen as the first substrates. In addition to these lactols, two other alkyl (2-hydroxytetrahydrofuran-2-yl)acetates, **6b** and **6c**, and alkyl (2-hydroxy-3,4,5,6-tetrahydropyran-2-yl)acetate **6e** were newly prepared from lactones **4b**, **4c** and **4e**[10] according to the procedure of Dugan *et al.* as the substrates for the intercalation. Some of these lactols comprised a tautomeric mixture of the lactol form (7–8 parts) and the corresponding ring-opened hydroxy keto ester (3–2 parts), as indicated by their ^1H NMR spectra.

Ring Expansions of the γ- and δ-Lactol Derivatives **6a–e**.—A selective radical cleavage of the lactol ring was carried out according to the procedure previously published by us; irradiation of an equilibrated mixture of lactol **6a** and the corresponding hydroxy keto ester in benzene containing mercury(II) oxide and iodine (2 mol equiv. each) with a 100 W high-pressure Hg arc through a Pyrex-filter at room temperature gave the ω-iodoalkyl diester **7a** resulting from endocyclic cleavage in 45% yield, along with *tert*-butyl iodoacetate resulting from exocyclic cleavage in 9% yield. A similar photolysis of an equilibrated mixture of lactol–hydroxy ketones **6b**, **c** and lactols **6d**, **e** gave ω-iodoalkyl diesters **7b–e** as the major products in 33–70% yield along with an accompanying formation of alkyl iodo acetates (11 and 7% in the case of **6b** and **6c**).

It should be noted that endocyclic cleavage of alkoxyl radicals generated from the lactols takes place in preference to exocyclic cleavage in this β-scission reaction. Since the exocyclic cleavage gives stabilized radicals, $\cdot CH_2CO_2R$, this β-scission seems to be a kinetically controlled process.

The heating of ω-iodoalkyl propanedioate **7a** in benzene



4, 6, 7 and **9a** $n = 0$, $R^1 = R^2 = H$, $R^3 = Bu^t$
b $n = 0$, $R^1 = R^2 = H$, $R^3 = Et$
c $n = 0$, $R^1 = Me$, $R^2 = H$, $R^3 = Bu^t$
d $n = 1$, $R^1 = R^2 = H$, $R^3 = Bu^t$
e $n = 1$, $R^1 = R^2 = -(CH_2)_4-$, $R^3 = Bu^t$

5 and **8a** $R^3 = Bu^t$
b $R^3 = Et$
10a $R^1 = H$, $R^4 = PhCH_2$
b $R^1 = R^4 = Me$

Scheme 2 *Reagents and conditions:* i, $HgO–I_2$; ii, *hv*; iii, NaH–Et_4N^+ Br^-–benzene, reflux; iv, $C_6H_5CH_2Br$ or MeI; v, CF_3CO_2H, reflux

Table 1

	n	R^1	R^2	R^3	**6** (%)[a]	**7** (%)[b]	**9** (%)[b]
a	0	H	H	Bu^t	95[c]	45[d]	70
b	0	H	H	Et	45	33[e]	61
c	0	Me	H	Bu^t	76	39[f]	86
d	1	H	H	Bu^t	73	70	*g*
e	1		$-(CH_2)_4-$[h]	Bu^t	62	69	65

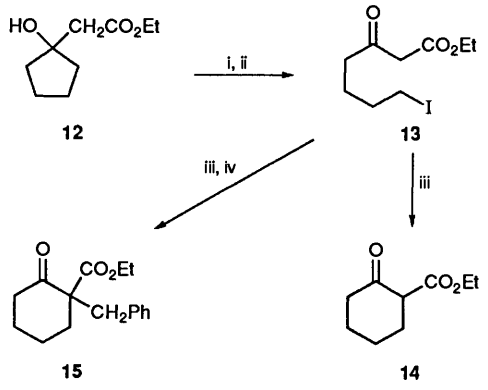
[a] Isolated yield by distillation. [b] Isolated yield by PLC. [c] Ref. 1. [d] *tert*-Butyl iodoacetate (9%) was formed as a by-product. [e] Ethyl iodoacetate (11%) was formed as a by-product. [f] *tert*-Butyl iodoacetate (7%) was formed as a by-product. [g] Intractable mixture. [h] Ref. 8.

containing tetraethylammonium bromide (1 mol equiv.) and sodium hydride (2 mol equiv.) under reflux, followed by the usual work-up (including preparative TLC of the product) gave 3,4,5,6-tetrahydro-2-oxo-2*H*-pyran-3-carboxylate **9a** in 70% yield. A similar treatment of ω-iodoalkyl propanedioate **7b**, **7c** and **7e** in benzene with tetraethylammonium bromide and sodium hydride gave the corresponding δ- and ε-lactones **9b**, **9c** and **9e**, in 61–86% yields, respectively. The attempted cyclization of ω-iodoalkyl propanedioate **7d** under conditions similar to those mentioned above, however, resulted only in the formation of an intractable mixture. Yields for the preparation of compounds **6**, **7** and **9** are given in Table 1.

α-Substituted δ-lactones can be prepared from γ-lactones by the present method; ω-iodoalkyl propanedioate **7a** in benzene containing tetraethylammonium bromide and sodium hydride was cyclized by heating under reflux, after which benzyl bromide was added. Heating the solution under reflux gave *tert*-butyl 3-benzyl 3,4,5,6-tetrahydro-2-oxo-2*H*-pyran-3-carboxylate **10a** in 61% yield.

Similarly, a mixture of diastereoisomers of α-disubstituted δ-lactone **10b** was obtained in 65% yield from ω-iodoalkyl propanedioate **7c**. Heating a solution of α-disubstituted δ-lactone **10a** in trifluoroacetic acid gave 3-benzyl-3,4,5,6-tetrahydropyran-2-one **11**[11] in 92% yield.

New Ring Expansion of Cyclopentanone to an α-Substituted Cyclohexanone.—The aforementioned method concerning the ring expansion of the γ- and δ-lactones can also be applied to the corresponding cyclic ketones. Thus, the submission of a substituted cyclopentanol **12**,[12] prepared from cyclopentanone, to the above-mentioned procedure gave ethyl 7-iodo-3-oxoheptanoate **13** in 46% yield. An endocyclic cleavage, which has been observed in the alkoxyl radicals generated from 1-methylcyclopentanol[13] and from cyclopentanol itself,[13b,14] is again favoured over exocyclic cleavage here, even though the stabilized radicals can be expelled in the latter process. Treatment of this ω-iodo keto ester **13** with tetraethylammonium bromide–sodium hydride gave ethyl 2-oxocyclohexanecarboxylate in 72% yield. On the other hand, successive treatment of ω-iodo keto ester **13** with tetraethylammonium bromide–sodium hydride and benzyl bromide gave ethyl 1-benzyl-2-oxocyclohexanecarboxylate **15** in 62% yield.



Scheme 3 *Reagents and conditions:* i, $HgO–I_2$; ii, *hv*; iii, NaH–Et_4N^+ Br^-; iv, $PhCH_2Br$

As mentioned above, since the ethoxycarbonyl group can readily be removed from 2-substituted 2-ethoxycarbonylcyclohexanone **15**, the present ring expansion can serve as a new method for the synthesis of 2-substituted cyclohexanones.

Experimental

IR spectra were determined with a JASCO IR-810 spectrophotometer. ^1H NMR spectra were determined in $CDCl_3$ ($SiMe_4$ as internal reference) with either an Hitachi R-90 FTNMR spectrometer operating at 90 MHz or a JEOL JNM-GX270 FT NMR spectrometer operating at 270 MHz. *J*-Values are given in Hz. High- and low-resolution mass spectra were recorded with a JEOL JMS-DX 303 spectrometer. TLC was carried out on Merck Kieselgel 60 PF_{254}. Photolysis was carried out with a 100 W high-pressure Hg arc lamp (EIKOSHA, EHB-WU-100).

α-Substituted Lactols **6**.—Lactols **6a** and **6d** were prepared by the procedure reported by Dugan *et al.*[9] The other lactols **6b**, **6c** and **6e** were also prepared according to their method.

Ethyl (*2-hydroxytetrahydrofuran-2-yl*)*acetate* (n = 0, $R^1 = R^2 = H$, $R^3 = Et$) **6b**. A tautomeric mixture with the corresponding hydroxy keto ester (*ca.* 7:3); b.p. 140 °C (bath temp.)/0.8 Torr;* ν_{max}(neat)/cm^{-1} 3400, 1735 and 1715; δ(90

* 1 Torr = 133.3 Pa.

MHz) 1.29 (3 H, t, *J* 7.04, OCH_2CH_3), 1.6–3.0 (6.1 H, m), 3.46 (0.6 H, s, active methylene of hydroxy keto ester), 3.66 (0.6 H, t, *J* 5.93, CH_2OH of hydroxy keto ester) and 3.9–4.6 (3.7 H, m); *m/z* 174 (M^+, 1.1), 156 [$(M - H_2O)^+$, 19] and 87 (100) (Found: M^+, 174.0899. $C_8H_{14}O_4$ requires *M*, 174.0892).

tert-*Butyl* (*2-hydroxy-5-methyltetrahydrofuran-2-yl*)*acetate* (n = 0, R^1 = Me, R^2 = H, R^3 = Bu^t) **6c**. A tautomeric mixture with the corresponding hydroxy keto ester (*ca.* 8:2); b.p. 105 °C (bath temp.)/0.55 Torr; ν_{max}(neat)/cm^{-1} 3450, 1730sh and 1710; δ(90 MHz) 1.20 (2.4 H, d, *J* 6.15, 5-Me of lactol), 1.32 (0.6 H, d, *J* 6.38, CH*Me*–OH of hydroxy keto ester), 1.48 (9 H, s, Bu^t), 1.7–2.7 (5.4 H, m), 3.37 (0.6 H, s, active methylene of hydroxy keto ester) and 4.0–4.8 (2 H, m); *m/z* 198 [$(M - H_2O)^+$, 1.7], 160 [$(M - Bu^t)^+$, 2.4], 101 [$(CO_2Bu^t)^+$, 56] and 57 (Bu^{t+}, 100) [(Found: M^+, 198.1248. $C_{11}H_{18}O_3$ requires $(M - H_2O)^+$, 198.1255].

tert-*Butyl* 2-*hydroxy*-3,4,4a,5,6,7,8,8a-*octahydro*-2H-1-*benzopyran-2-yl*)*acetate* [n = 1, R^1, R^2 = $-(CH_2)_4-$, R^3 = Bu^t] **6e**. A mixture of stereoisomers; b.p. 160 °C (bath temp.)/0.3 Torr; ν_{max}(neat)/cm^{-1} 3450 and 1710; δ(90 MHz), 0.9–1.9 (22 H, m, containing s at 1.47), 2.48 (2 H, s, $CH_2CO_2Bu^t$), 3.3–3.6 (0.5 H, m, 8a-H of one stereoisomer) and 4.1–4.2 (0.5 H, m, 8a-H of another stereoisomer); *m/z* 270 (M^+, 0.3), 252 [$(M - H_2O)^+$, 1.2] and 57 (Bu^{t+}, 100) (Found: M^+, 270.1832. $C_{15}H_{26}O_4$ requires M^+, 270.1831).

tert-*Butyl* 3-*Iodopropyl Propanedioate* (n = 0, R^1 = R^2 = H, R^3 = Bu^t) **7a**. *General Procedure for* β-*Scission of Lactols* **6**.—A stirred solution of hemiacetal **6a** (202 mg, 1 mmol) in benzene (15 cm^3) containing HgO (433 mg, 2 mmol) and iodine (504 mg, 2 mmol) in a Pyrex vessel was irradiated with a 100 W high-pressure Hg arc for 3 h in an atmosphere of nitrogen. The mixture was then filtered through a Celite pad. After the filtrate had been washed with 5% aqueous Na_2SO_3 and then water, it was dried over anhydrous $MgSO_4$, and then evaporated. The residual oil was purified by PLC on silica gel to afford the title compound **7a** (148 mg, 45%) together with *tert*-butyl iodoacetate (22 mg, 9%). **7a**: R_f 0.24 (1:10 EtOAc–hexane); an oil; ν_{max}(neat)/cm^{-1} 1740sh and 1730; δ(90 MHz), 1.47 (9 H, s, Bu^t), 2.0–2.3 (2 H, m, $OCH_2CH_2CH_2I$), 3.23 (2 H, t, *J* 6.82, CH_2I), 3.29 (2 H, s, active methylene) and 4.22 (2 H, t, *J* 5.94, CO_2CH_2); *m/z* 328 (M^+, 0.1), 201 [$(M - I)^+$, 12], 57 (Bu^{t+}, 100) (Found: M^+, 328.0170. $C_{10}H_{17}IO_4$ requires *M*, 328.0172).

Ethyl 3-*iodopropyl propanedioate* (n = 0, R^1 = R^2 = H, R^3 = Et) **7b**. Irradiation for 5 h; R_f 0.43 (1:5 EtOAc–hexane); an oil; ν_{max}(neat)/cm^{-1} 1730; δ(90 MHz), 1.29 (3 H, t, *J* 7.25, OCH_2CH_3), 2.17 (2 H, quintet, *J* 6.4, $ICH_2CH_2CH_2O$), 3.23 (2 H, t, *J* 6.81, CH_2I), 3.38 (2 H, s, active methylene) and 4.1–4.4 (4 H, m, OCH_2CH_3 and CO_2CH_2); *m/z* 301 [$(M + 1)^+$, 1.9], 282 [$(M - H_2O)^+$, 19], 255 [$(M - OEt)^+$, 10], and 173 [$(M - I)^+$, 100] [Found: M^+, 300.9915. $C_8H_{14}IO_4$ requires $(M + 1)^+$, 300.9936].

tert-*Butyl* 3-*iodo*-1-*methylpropyl propanedioate* (n = 0, R^1 = Me, R^2 = H, R^3 = Bu^t) **7c**. irradiation for 6 h; R_F 0.58 (1:5 EtOAc–hexane); an oil; ν_{max}(neat)/cm^{-1} 1740sh and 1730; δ(90 MHz) 1.28 [3 H, d, *J* 6.18, $CH(CH_3)OCO$], 1.47 (9 H, s, Bu^t), 2.0–2.3 [2 H, m, $ICH_2CH_2CH(CH_3)O$], 3.16 (2 H, t, *J* 7.04, ICH_2), 3.27 (2 H, s, active methylene) and 4.8–5.2 [1 H, m, $CH(CH_3)OCO$]; *m/z* 269 [$(M - OBu^t)^+$, 7.1], 215 [$(M - I)^+$, 11], 159 (28) and 57 (100) [Found: M^+, 268.9687. $C_7H_{10}IO_3$ requires $(M - C_4H_9O)^+$, 268.9674].

tert-*Butyl* 4-*iodobutylpropanedioate* (n = 1, R^1 = R^2 = H, R^3 = Bu^t) **7d**. Irradiation for 3 h; R_f 0.55 (1:3 EtOAc–hexane); an oil; ν_{max}(neat)/cm^{-1} 1753; δ(90 MHz) 1.47 (9 H, s, Bu^t), 1.5–2.1 [4 H, m, $ICH_2(CH_2)_2CH_2O$], 3.21 (2 H, t, *J* 7.03, ICH_2), 3.28 (2 H, s, active methylene) and 4.16 (2 H, t, *J* 5.30, CH_2O); *m/z* 342 (M^+, 0.1) 286 [$(M - C_4H_8)^+$, 8.9] and 57 (100) (Found: M^+, 342.0313. $C_{11}H_{19}IO_4$ requires *M*, 342.0328).

tert-*Butyl* 2-(*2-iodoethyl*)*cyclohexyl propanedioate* [n = 1, R^1, R^2 = $-(CH_2)_4-$, R^3 = Bu^t] **7e**. Irradiation for 2h; a mixture of stereoisomers; R_F 0.56 (1:5 EtOAc–hexane); an oil; ν_{max}(neat)/cm^{-1} 1725; δ(90 MHz) 1.1–2.1 (20 H, m, containing s at 1.45), 3.18 (2 H, t, *J* 5.86, ICH_2), 3.26 (2 H, s, active methylene) and 5.0–5.2 (1 H, m); *m/z* 340 [$(M - C_4H_8)^+$, 2.2] 213 (9.5) and 109 (100) (Found: M^+, 340.0170. $C_{11}H_{17}IO_4$ requires *M*, 340.0171).

tert-*Butyl* 3,4,5,6-*Tetrahydro*-2-*oxo*-2H-*pyran*-3-*carboxylate* (n = 0, R^1 = R^2 = H, R^3 = Bu^t) **9a**: *General Procedure for Intramolecular Cyclization of the Iodoalkyl Propanedioates* **7**.—To a stirred solution of **7a** (166 mg, 0.5 mmol) in benzene (10 cm^3) were added successively Et_4NBr (95 mg, 0.5 mmol) and NaH (50%, 48 mg, 1 mmol). The mixture was heated under reflux. After the completion of the reaction (*ca.* 1 h) the solution was cooled and poured into aq. NH_4Cl. The organic layer was separated, washed with brine, and dried over anhydrous $MgSO_4$. Evaporation of the solvent gave a crude oil which was purified by PLC on SiO_2 to afford the title compound **9a** (70 mg, 70%); R_F 0.23 (CH_2Cl_2); an oil; ν_{max}(neat)/cm^{-1} 1720; δ(90 MHz) 1.49 (9 H, s, Bu^t), 1.6–2.3 (4 H, m, 4- and 5-H), 3.46 (1 H, t, *J* 7.47, 3-H) and 4.34 (2 H, t, *J* 5.5, 6-H); *m/z* 199 [$(M - 1)^+$, 0.1], 145 [$(M - C_4H_8)^+$, 13], 127 (36) and 57 (100) [Found: M^+, 199.0992. $C_{10}H_{15}O_4$ requires $(M - 1)^+$, 199.0970].

Ethyl 3,4,5,6-*tetrahydro*-2-*oxo*-2H-*pyran*-3-*carboxylate* (n = 0, R^1 = R^2 = H, R^3 = Et) **9b**. R_f 0.45 (1:1 EtOAc–hexane); an oil; ν_{max}(neat)/cm^{-1} 1725; δ(90 MHz) 1.30 (3 H, t, *J* 7.03, OCH_2CH_3), 1.6–2.4 (4 H, m, 4- and 5-H), 3.56 (1 H, t, *J* 7.47, 3-H), 4.15–4.45 (4 H, m, OCH_2CH_3 and 6-H); *m/z* 172 (M^+, 5.6), 127 [$(M - OEt)^+$, 37] and 100 [$(M - CO_2Et)^+$, 85] and 55 (100) (Found: M^+, 172.0748. $C_8H_{12}O_4$ requires *M*, 172.0735).

tert-*Butyl* 3,4,5,6-*tetrahydro*-6-*methyl*-2-*oxo*-2H-*pyran*-3-*carboxylate* (n = 0, R^1 = Me, R^2 = H, R^3 = Bu^t) **9c**. A mixture of diastereoisomers; R_F 0.46 (1:3 EtOAc–hexane); ν_{max}(neat)/cm^{-1} 1720; δ(90 MHz) 1.37 and 1.39 (combined 3 H, 2d, *J* 6.18, each, 6-Me), 1.49 (9 H, s, Bu^t), 1.6–2.3 (4 H, m, 4- and 5-H), 3.2–3.6 (1 H, m, 3-H) and 4.3–4.6 (1 H, m, 6-H); *m/z* 199 [$(Me - Me)^+$, 1.7], 159 [$(M - C_4H_8)^+$, 11], 141 [$(M - OBu^t)^+$, 20] and 57 (100) [Found: M^+, 199.1101. $C_{10}H_{15}O_4$ requires $(M - CH_3)^+$, 199. 1107].

tert-*Butyl*2,3,4,5,5a,6,7,8,9,9a-*decahydro*-2-*oxobenzyl*[1]*oxepine*-3-*carboxylate* [n = 1, R^1, R^2 = $-(CH_2)_4-$, R^3 = Bu^t] **9e**. A mixture of diastereoisomers; R_F 0.48 (1:3 EtOAc–hexane); ν_{max}(neat)/cm^{-1} 1735; δ(90 MHz) 0.9–2.5 (22 H, m containing s at 1.49) and 3.0–5.1 (2 H, m, 3-, 9a-H); *m/z* 195 [$(M - OBu^t)^+$, 9.9] 177 (13), 108 (22) and 57 (100) [Found: M^+, 195.1177. $C_{11}H_{15}O_3$ requires $(M - C_4H_9O)^+$, 195.1158].

tert-*Butyl* 3-*Benzyl*-3,4,5,6-*tetrahydro*-2-*oxo*-2H-*pyran*-3-*carboxylate* (R^1 = H, R^4 = CH_2Ph) **10a**.—A mixture of iodoalkyl malonate **7a** (131 mg, 0.4 mmol), Et_4NBr (152 mg, 0.8 mmol) and NaH (50%, 43 mg, 0.9 mmol) in benzene (8 cm^3) was heated under reflux for 1 h, as described above. Methyl iodide (71 mg, 0.5 mmol) was then added to the reaction mixture, and the solution was heated under reflux for an additional 30 min. The usual work-up and purification as that mentioned above gave the title compound **10a** (71 mg, 61%); R_F 0.36 (1:5 EtOAc–hexane); ν_{max}(neat)/cm^{-1} 1727; δ(90 MHz) 1.47 (9 H, s, Bu^t), 1.5–2.2 (4 H, m, 4- and 5-H), 3.05 (1 H, d, *J* 13.63, benzylic), 3.49 (1 H, d, *J* 13.63, benzylic), 3.8–4.3 (2 H, m, 6-H) and 7.24 (5 H, m, aromatic); *m/z* 290 (M^+, 0.17), 234 [$(M - C_4H_8)^+$, 70] and 189 [$(M - CO_2Bu^t)^+$, 100] (Found: M^+, 290.1525. $C_{17}H_{22}O_4$ requires *M*, 290.1518).

tert-*Butyl* 3,4,5,6-*tetrahydro*-3,6-*dimethyl*-2-*oxo*-2H-*pyran*-3-*carboxylate* (R^1 = R^4 = Me) **10b**. This compound was ob-

tained by the same procedure as mentioned above as a mixture of diastereoisomers; R_F 0.46 (1:3 EtOAc–hexane); ν_{max}(neat)/cm^{-1} 1725; δ(90 MHz) 1.3–2.3 (19 H, m containing s at 1.47) and 4.3–4.6 (1 H, m, 6-H); *m/z* 213 [(M − Me)$^+$, 0.5], 155 [(M − OBu^t, 5.3], 128 (14) and 57 (100) [Found: M$^+$, 213.1113. $C_{11}H_{17}O_4$ requires $(M - CH_3)^+$, 213.1127].

3-*Benzyl*-3,4,5,6-*tetrahydropyran*-2-*one* **11**.[12]—A solution of lactone **10a** (45 mg, 0.16 mmol) in CF_3CO_2H (1 cm^3) was stirred for 2.5 h at room temperature and then heated under reflux for 45 min. After cooling, trifluoroacetic acid was removed under reduced pressure. Purification of the residue by PLC on SiO_2 gave compound **11** (28 mg, 92%); R_F 0.17 (1:3 EtOAc–hexane).

Ethyl 7-*Iodo*-3-*oxoheptanoate* **13**.—β-Scission of hydroxy ester **12**[10] was carried out in a similar manner as described for the β-scission of lactols **6** to give the title compound **13** (irradiation for 6 h). A keto-enol mixture; R_f 0.39 (1:5 EtOAc–hexane); ν_{max}(neat)/cm^{-1} 3450, 1735, 1710 and 1635; δ(90 MHz) 1.28 (3 H, t, *J* 7.25, OCH_2CH_3), 1.6–1.9 (m, 4 H, 5- and 6-H), 2.4–2.7 (2 H, m, 4-H), 3.18 (2 H, t, *J* 6.58, $-CH_2I$), 3.43 (1.6 H, s, $COCH_2CO$), 4.20 (2 H, q, *J* 7.25, OCH_2CH_3), 4.98 (0.2 H, s, vinylic H of enol form) and 12.10 (0.2 H, s, OH of enol form); *m/z* 298 (M$^+$, 0.7), 171 [(M − I)$^+$, 73] and 55 (100) (Found: M$^+$, 298.0058. $C_9H_{15}IO_3$ requires, *M*, 298.0066).

Ethyl 2-*Oxocyclohexanecarboxylate* **14**.—This compound was prepared by the same procedure described for the transformation of iodoalkyl malonate **7a** into lactone **9b** using ester **13** as the starting material and identified by a direct comparison with a commercially obtainable sample.

Ethyl 1-*Benzyl*-2-*oxocyclohexanecarboxylate* **15**.—This compound was obtained by the same procedure as described for the preparation of lactone **10a** using ester **13** as the starting material; R_F 0.45 (1:5 EtOAc–hexane); an oil; ν_{max}(neat)/cm^{-1} 1735 and 1710; δ(90 MHz) 1.16 (3 H, t, *J* 7.25, OCH_2CH_3), 1.3–2.0 (6 H, m), 2.2–2.6 (2 H, m, 3-H), 2.86 (1 H, d, *J* 13.84, benzylic H), 3.32 (1 H, d, *J* 13.84, benzylic H) 4.09 (2 H, q, *J* 7.25, OCH_2CH_3) and 7.0–7.4 (5 H, m); *m/z* 260 (M$^+$, 8.9), 187 [(M − CO_2Et)$^+$, 36] and 91 [(M − CH_2Ph)$^+$, 100] (Found: M$^+$, 260.1408. $C_{16}H_{20}O_3$ requires *M*, 260.1411).

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